Chapter 6
Recovery of Various Metals from Industrial Wastewater by Biological Methods

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Abstract Industrial wastewater contains a variety of hazardous chemicals as well as high metal concentrations. Metal-contaminated wastewater is hazardous to the environment and can have serious health consequences if it enters biological systems. However, the recovery of metals from wastewater can increase the sustainability of treatment processes and enhance cost-effectiveness. There are numerous conventional treatment methods for recovering metals from wastewater, including physical, chemical, and even biological methods. Physical and chemical processes are primarily energy and chemical-intensive. New-age research uses novel bio-recovery methods to extract and remove metals from wastewater. Various methods like sorption, biomembranes, bioelectrochemical techniques, etc., have been discussed in this chapter in a summarized form. Further, insights into energy-efficient recovery methods and their applications have been elaborated.

Keywords Bio-recovery · Bioleaching · Bioelectrochemical · Sorption · Biochemical

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6.1 Introduction

Water, which has always been an essential constituent of the living system, has been depleted to a great extent, and hence, the present time demands recycle and reuse of water from wastewater. Not only this many naturally occurring minerals and resources are also decreasing rapidly and, therefore, need serious attention. Resource recovery has gained momentum in recent times due to the limited availability of natural resources. Even though this is not a new process and has been in the application at many wastewater treatment facilities in European countries (Meena et al. 2019). Metals have been an important part of society for ages and hold historical significance. Heavy industrialization has increased a tremendous demand for heavy metals, and with ever-increasing demands, there is an anti-parallel depletion in the availability of these metals. The increasing need for important metals drawn tremendous attention because of their severe scarcity, least substitutability, and high degree of unequal distribution. The present time is looking for alternate sources of these metals. Recovery of metals from the wastes is one such alternative that serves the dual role in metal extraction and environmental cleansing (Jadhav and Hocheng 2012; Moss et al. 2011). Wastewater discharged from various industries like mining and metallurgy, tanneries, semiconductor and alloys manufacturing units, plastic manufacturing units, anticorrosive agents, dyes and pigments, batteries, and electroplating contains a heavy dose of metals, especially transition metals. Hence, they also serve as a great source of metal recovery from wastewater. Low pH, reduced COD, and higher dosages of heavy and toxic metals tend to be some of the important properties of such wastewater. Most of these metals are toxic and are present in high concentrations. However, suitable methods may be applied to recover these metals by reducing their toxicity and converting them into insoluble forms (Kumar et al. 2021). Heavy metals, unlike organic pollutants, are redundant and non-biodegradable, highly toxic, and bioaccumulate in living tissues, allowing them to pass through generations. Nearly 60% of the world's population affected by pollution is because of heavy metal toxicity. Most of these heavy metal pollutants include Hg, Cd, Cu, Ag, Pb, Zn, and Co. Electroplating industries in China generate more than 4 billion tons of heavy metal-loaded wastewater (Sahinkaya et al. 2017). These metals if not removed can tend to leach into groundwater or move across biological systems which highlight a serious need for their removal from wastewater. Metal pollutants are highly carcinogenic and quite damaging to living systems. Not only this, their free discharge into the living system led to serious loss the natural resources too. Various kinds of metals that are present in wastewater are—Cu (electronic and metal finishing wastes), Zn (electronic and metallurgical wastes), Ni (petrochemical refineries), Pb (automobile industries), Ag and Au (electronic wastes), etc. (Chmielewski et al. 1997).

Several available technologies such as adsorption, chemical precipitation, ion-exchange, reverse-osmosis, electrofiltration, electrosorption, electrodialysis, coagulation and membrane filtration have been applied with success in the removal of toxic and heavy metals from wastewater. However, these methods, though highly effective, had certain drawbacks such as high economic investments, larger chemical and reagent wastage, non-specific removal of metal ions, high energy requirements and sludge as well as secondary contaminant generations (Amanze et al. 2022; Khulbe and Matsuura 2018). Metal bio-recovery is not a new concept and it has also been part of biomining activities in the past as well as the bioremediation of heavy metals and their ions from industrial wastewater. The combined knowledge of biomining and bioremediation has been successfully used up in the bio-recovery processes. While biomining involves processes such as bioleaching through chelation, bioaccumulation (use of living microbes to take up metals intracellularly), acidification and oxidation (microbe-assisted oxidation–reduction reactions of metals used for metal detoxification) which is mainly a process of metal mobilization; methods like bioreduction, bioprecipitation and biosorption form an integral part of bioremediation technology (Puyol et al. 2017).

Extraction of metals from wastewater is a tedious task as the metal concentration is quite low. Especially, the physicochemical techniques pose serious challenges in case of low or very low concentrations. Bio-recovery processes play a heroic role in such situations. Even if numerous techniques are available for removal and recovery of metals from industrial wastewater, biological and biotechnical methods are one of the most promising and highly efficient techniques. Microbial techniques are not only energy-efficient but also environmentally friendly. They show high specificity while targeting metal ions as they are mostly enzyme-dependent in action. They do not require highly acidic or alkaline conditions for their operations which reduces chemical wastage. In a way, they are mostly part of healthy, robust and sustainable environmental remediation methods. This chapter explores various critical aspects of conventional techniques for the removal and recovery of metals from wastewater and spans over various bio-recovery processes that can be applied. Attention has also been drawn towards the limitations of these methods and plausible solutions for overcoming problems.

6.2 Metal Recovery from Wastewater Using Conventional Methods

Recovery of heavy metals from industrial wastewater is not a very recent technology but a very old and established practice in treatment technology. They have been classified into physical (membrane filtration, ion-exchange, solvent extraction) and chemical methodologies (precipitation, electrodeposition, coagulation, photocatalysis and complexation) and sometimes even physicochemical (adsorption). Techniques such as micro-, nano- and ultrafiltration as well as Reverse osmosis depends on the application of pressure and membrane to retain elemental metals or metal ions from their aqueous solutions. Chemically-modified membranes are also used as sorbents for the selective removal of heavy metals from wastewater. Polycysteine-functionalized microfiltration membranes have been found to be effective in the removal of Hg and Cd (Ritchie et al. 2001). Physical separation techniques are mainly applicable to metals present in particulate form. These processes are mainly involving hydrodynamic application, mechanical screening techniques, scrubbing, gravity separation, magnetic separation etc. However, these processes are limited to certain optimum conditions and are mainly dependent on the particle size of metals. Moreover, physical processes cannot be applied in cases of low concentrations of metals present in aqeuous solutions (Fu and Wang 2011). Because of its ease of operation and simple handling, the precipitation method is the most commonly used chemical technique in the removal of heavy metals from industrial wastewater. It mainly targets the conversion of heavy metals into their oxides, hydroxides, carbonates, sulphides, sulphates, phosphates etc. It is followed by coagulation and flocculation for the separation of metal salts from wastewater. Removal efficiency can easily be enhanced by changing and tuning the pH and hence separating different metals at different pH (Ku and Jung 2001). The coagulation and flocculation of metal precipitates mainly depend on their zeta potential (ζ; electrostatic interaction between metals and flocculating agents). The electrochemical treatment method is the process where metals are deposited on the surface of electrodes by applying an electric current between them. These electrodes are dipped in a metal-containing solution and the anode used is insoluble. Various types of electrochemical methods that are used in the recovery of heavy metals from wastewater are electrodeposition, electrooxidation and electrocoagulation (Shim et al. 2014). Factors such as temperature, pH, metal concentration, and the presence of interfering radicals in wastewater all have a significant impact on chemical processes. Ion-exchange process is mainly a process of ion-uptake from their aqueous solution into a solid substrate and is one the most significant methodology used in water treatment industries. It is a cost-effective, easily operative and highly effective method applied in the separation of heavy metals even at minute concentration. Ion-exchanger resins are used for the exchange of cations and anions which are water-insoluble solid substrates capable of absorbing positive or negative ions from their electrolytic solutions (Hamdaoui 2009).

Membrane filtration and ultrafiltration remove heavy metals from their solution through a size-dependent separation technique. The ultrafiltration method uses a permeable membrane of pore size 5–20 nm and has 90% removal efficiency. Polymer-supported ultrafiltration is the addition of water-soluble polymer-based ligands that produce macromolecular complexes in interaction with metal ions. They are well-known for their high selectivity, low-energy consumption and faster kinetics (Trivunac and Stevanovic 2006). Another membrane-based separation technique is Reverse-Osmosis (RO) where pressure is applied to force metal-containing solution. The membrane retains metal on one-side and solvent passes through the membrane through a diffusion-mechanism. The process of separation depends on the concentration of solute, pressure applied on the membrane and flux-rate (Sarai Atab et al. 2016). Electrodialysis is a highly effective membrane technology that involves passing ionised species in an aqueous solution through an ion-exchange membrane using an electric potential. On passing through cell compartments the anion migrates towards the anode and cations migrate towards the cathode by passing through the ion-exchange membranes (Robeson 2012). The major disadvantage of this technique is the corrosion of the membrane. Other factors that affect electrodialysis are flow rate, temperature and electrode potential applied at different concentrations. All these methods have their own advantages and disadvantages. The major drawback of these techniques lies in their high-energy application. Membrane-based techniques are quite viable and are highly effective in the removal of metal ions but they still it hold some serious drawbacks. The problem of membrane fouling is one of the most serious and needs proper consideration while application. They have a high cost of application due to high energy consumption. Similarly, ion-exchange resins though highly effective are limited in their applications are limited in solutions with higher metal concentrations. Because of its high surface area and ease of availability, activated carbon is one of the most affordable heavy metal adsorption alternatives. It has a tendency to adsorb various metals such as Ni, Cu, Hg, Zn, Fe, etc. Now adays even wastes such as rice husk ash and fly ash as used as sorbents in the removal of metals from wastewater (Wang and Ren 2014). To overcome the shortcomings of various treatment methods it was necessary to devise some technique which is highly selective, cost-effective and uses natural sources for their operation. Hence, bio-recovery is a new method which is discussed here. It primarily employs plants, their biomasses, and microbial systems for heavy metal removal and recovery from wastewater.

6.3 Biological Methods of Recovery

6.3.1 Bioelectrochemical

Bioelectrochemical system (BES) stands as one of the cleanest and most novel water treatment methods for biorecovery of metals from wastewater. It is a new-age bioengineering technique that generates electrical energy from the chemical energy of biomass by the application of biocatalysts which are mainly exoelectrogenic microorganisms (Syed et al. 2021). BES is a fundamental technology that uses microorganisms to convert chemical energy stored in biomass into electrical energy and chemicals. Because of its ability to provide a common platform for oxidation and reduction-oriented processes, it serves the dual purpose of waste treatment and electricity generation at the same time, as well as resource recovery (Wang and Ren 2014). It is mainly known for its high efficiency, reduced energy consumption and environmentally friendly applications. Furthermore, they function under anaerobic conditions by degrading organic matter via exoelectrogens. These release electrons which move towards the anode by an external circuit and hence electricity is generated (Li et al. 2008; Nancharaiah et al., 2015). A classical BES reactor system constitutes a pair of anode and cathode and an optical separator. The BES system configurations vary as per their target pollutants. Wastewater is oxidized in the anodic chamber by the microbes and generates a current at the cathode. These electrons in the cathode chamber are either used for the direct generation of electricity as common in MFC or oxidize chemicals such as metal ions or organic compounds (Wang and Ren 2014; Wang and Ren 2013).

There are four mechanisms which have been reported for the bioelectrochemical recovery of metals from wastewater as shown in Fig. 6.1. Out of this first method is the direct recovery of metals from wastewater through an abiotic cathode (Fig. 6.1a) using a Normal hydrogen electrode using electron donors and target metals are mostly Cd(II), Cu(II), Fe(III) and Zn(II); the second method is the recovery of metal using abiotic cathodes provided with external sources of energy (Fig. 6.1b) and targets metals with lower redox potentials mainly Ni(II), Cu(II), Pb(II), Cd(II) and Zn(II); the third one is the conversion of metal by bio-cathodes (Fig. 6.1c) and targets Cr(VI), Au(III), As(V), Ag(I), Se(VI) and Se(IV) using a dissimilatory metal reducing bacteria (DMRB) such as *Trichococcus pasteurii, Pseudomonas aeruginosa, Aspergillus niger, Geobacter sulfurreducens, Clostridium,* etc.; and the fourth mechanism is the conversion of metal by bio-cathode with external energy supply (Fig. 6.1d) and targets metals with lower redox potentials and external power sources promotes reduction for metals such as U(VI) and Cr(IV) by bacteria *Geobacter sulfurreducens.* From a microbial fuel cell, exoelectrogenic strains of Castellaniella sp. A5, B3, and A3 were isolated (MFC) and used as bioelectrochemical systems for the generation of bioelectricity and hence can be used in the treatment of industrial wastewater in pure as well as mixed form. They were discovered to be extremely effective at removing Cu, Cd, and Cr metals, with removal efficiencies of 99.8, 99.91, and 99.59, respectively. A microbial-assisted electrochemical system was used to reduce the Cr and Cu in industrial wastewater [which were present in the form of Cr(VI) and Cu(II)]. In the case of Cd(II), precipitation was either in the form of hydroxide or carbonate (Amanze et al. 2022).

6.3.2 Bioprecipitation/Biomineralization

Biomineralization/Bioprecipitation is mainly a process of immobilization of soluble metals into solid forms. Bioprecipitation of metals in wastewater is mainly done using microorganisms through detoxification methods. This technique promotes the removal of metals from their aqueous solutions through solid precipitate and then filtering out by simple solid–liquid extraction (Ike et al. 2017). Fungal metal biorecovery is a novel, cost-effective and highly efficient technology for metal processing, especially for the extraction of cobalt and nickel. *Aspergillus niger has been studied for its ability to biorecover Co and Ni from their phosphates and oxalates.* The use of extracellular polymeric substances promoted the precipitation of these metal ions. Extracellular polymeric substances (proteins or polysaccharides) play a critical role in bioprecipitation processes. They control and regulate nucleation and crystal growth (Yang et al. 2020; Ferrier et al. 2021). A typical bioprecipitation involves the reduction of metals to their lower oxidation states and hence slowing down their mobility. Sometimes, they are even transformed into their elemental forms. The reductive degradation of Se(VI) and Se(IV) to Se(0) using the bacterium Thauera

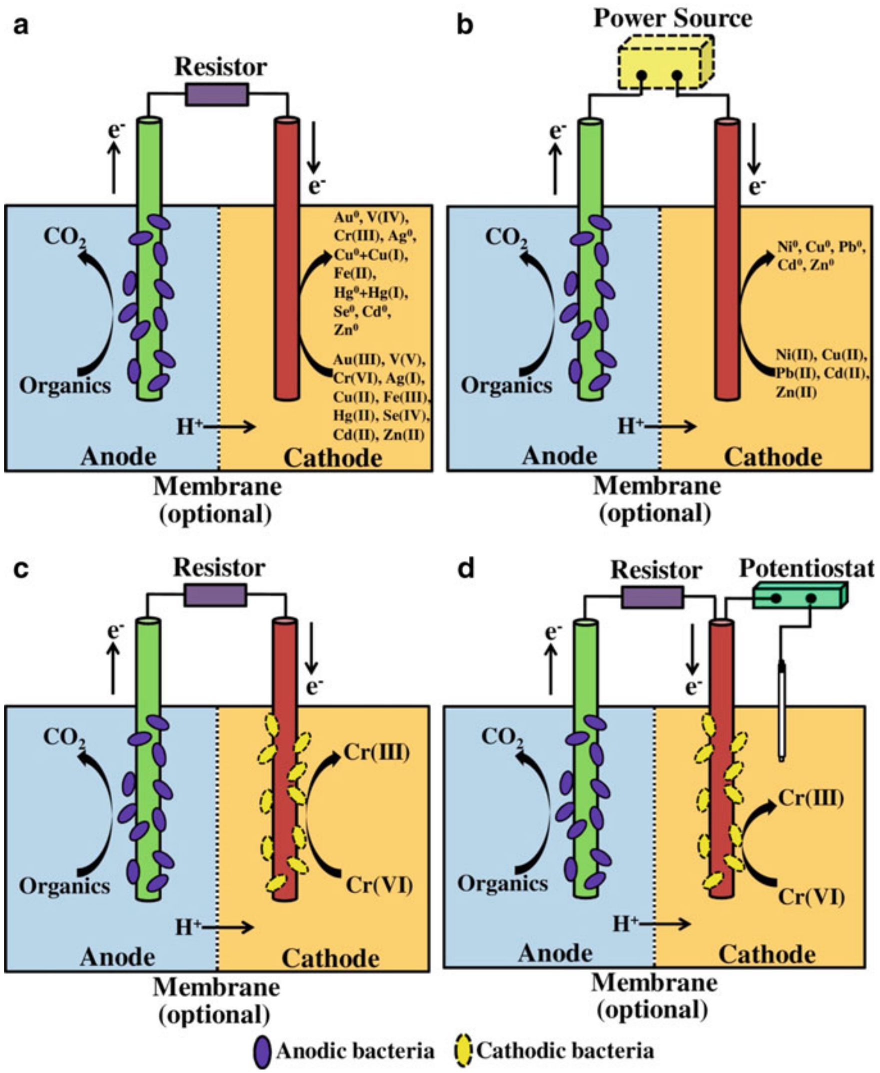

Fig. 6.1 Types of bioelectrochemical systems for biorecovery of metals and their mechanisms [Reprint permissions received]

selanatis has been successfully applied in cleaning drainage water (Cantafio et al. 1996). *Lysinibacillus* has been found to immobilize Pb(II) at a pH of 2 and the best part of using this bacteria is achieving reusability of bacteria (Zhang et al. 2022). *Lysinibacillus fusiformis* DB1-3 bacteria has been applied in the biomineralization of calcium carbonate and magnesium carbonate and leading to the precipitation of these metal ions (Yan et al. 2020). *Bacillus cercus* has an unusual speciality of precipitating Pb(II). In this process of biomineralization, cysteine is degraded intracellularly to

Fig. 6.2 Synthesis of TATS@AC [Reprint with Permission; Naushad et al. 2020]

H_2S which travels to the cell surface and reacts with Pb(II) leading to the formation of PbS (Staicu et al. 2020).

Biological sulphide precipitation is an efficient method for heavy metal biorecovery from wastewater. It mainly employs sulphate-reducing bacteria and the major advantages of this technique are low cost of application, formation of insoluble salts as precipitates and effectiveness at even very low concentrations. Sulphate reduction even under anaerobic conditions is one of the major benefits provided by this method. One such application of SRB is the generation of CdS nanocomposites through biomineralization using biomolecules as precipitating agents and then its further application in the photocatalysis of tetracycline which is an organic pollutant pharmaceutical waste (Ren et al. 2020). *Alcaligenes faecalis* K2 has been found effective in the biomineralization of Cd(II) with an efficiency of 85.5%. The microbe produces Secretory Organo-Biominerals (SOBs) which act as highly effective adsorbent (Ye et al. 2021). The metal sulphides that are extracted in the Nanoscale can be applied in solar cells, photocatalytic dye degradation and electroplating. The removal of metal and its recovery is done either in a single step or multistep. Here are some of the salient features that prove the efficacy of SRB over other conventional techniques of recovery of metals (Kumar et al. 2021):

- Insoluble salts formation even at very low pH (2–3.5)
- Different solubility products of metals with Sulphide lead to high selectivity
- Precipitate settles easily, densely and easily dewatered
- Cost-effective method.

6.3.3 Biosorption

Biosorption is defined as the binding of metals or other chemical ions to the surface of biomolecules from their aqueous solutions (Gautam et al. 2012). It is mainly done using dead biomass as compared to other processes such as bioaccumulation.

This is one of the most well-known non-destructive biological treatment methods for removing recalcitrant compounds. This method mainly depends upon the affinity of sorbate (chemical) and the sorbent (biomass). Metals in wastewater are adsorbed on external polysaccharides, lipids and proteins that are present in the biomass. The biomolecules that are primarily involved in this process include lipopolysaccharides, proteins, peptidoglycans and phospholipids (Kikuchi and Tanaka 2012; Vijayaraghavan and Yun 2008). Temperature, pH, biomass loading, time of equilibrium, biological systems, and metal ion concentration in wastewater all are the factors that affect the sorption potential. Metal ions are adsorbed on the biomass materials through various interactions (Van der Waal, electrostatic, surface precipitation, complex formations or sometimes a combination of two or more forces may be involved). Biomass materials used in this process include a diverse range of biological systems such as bacteria, fungi, algae, plant tissues and wastes, shells of crabs, shrimps, or other sea animals, lichens, and seaweeds. These have been found to be excellent binding materials for metals and have been used as sorbents widely (Kikuchi and Tanaka 2012). Microbial and algal cell walls bind to the metal ions through complexation, electrostatic interactions or ion-exchange mechanisms. The surface of cell walls contains many active functional groups such as hydroxyl, amines, phosphates, carbonyls and carboxyl (Ahluwalia and Goyal 2007).

Some of the bacteria that are capable of biosorption of metals from the wastewater are: *Bacillus licheniformis* (Cr, Cd, Pb, Zn), *Bacillus firmus* (Pb, Cu, Zn), *B. coagulans* (Cr), *B. megaterium* (Cr), *Enterobacter* (Cd, Pb), *Alcaligenes* (Pb), *Ochrobactrum intermedium* (Cu, Cr) etc. (Jacob et al. 2018). Damodar river water was assessed for the presence of heavy metals and it was found to contain Cr(III), Fe(III), Co(II), Cu(II), Ag(I), Pb(II) etc. due to discharge from nearby industrial sources. This water was studied for metal uptake via biosorption using the bacterium Geobacillus thermodenitrificans (st. MTCC 8341), and metal sorption was highly affected by the initial concentration of metals as well as the pH of the sample solution (Chatterjee et al. 2010). Not only microorganisms have been used in biomass but plant materials hold importance too. Sunflower stalk wastes have been used in the adsorption of Cu(II), Zn(II), Cd(II), and Cr(III); coir pith was used in the adsorption of Co(II), Cr(III), and Ni(II); and chitosan was used in the removal of Cd(II) and Cr(III); all of these are examples of non-microbial biomass applications (Gautam et al. 2012). Some of the advantages that are offered by biosorption are a metabolically-mediated fast process with higher cost-effectiveness; easier recovery of metals from the loaded biomass with the use of simple chelating agents such as EDTA; higher performance due to easier physical and chemical treatment; wide range of applications and so on. Hence, biosorption is a great treatment process (Golnaraghi Ghomi et al. 2020).

6.3.4 Biomembranes

Membrane technology has been widely accepted as a treatment technique for wastewater. Many membrane-based remediation methods have been developed for the removal of organic and inorganic pollutants, and have been known for their application for a wide range of pollutants. Silica and zeolites-based biomembranes are very well-known for their diverse range of separation behaviour. Biomembranes are organically derived membranes for the separation of metals from wastewater. They are mainly plant- or animal-based biomasses such as cellulose, gelatin, hemicellulose, chitosan and lignin. The OH^- groups present on the surface of cellulose act as a perfect metal binder. The surface of cellulose is well modified for the adsorption of heavy metals. Polymer-Biomass nanocomposites are also a newly developed technique where polymers are grafted on the surface of biomass as per desired metal to be treated (Kaur et al. 2022). Polyethyleneimine-Grafted Gelatin Sponge has been used to remove lead and Cadmium from wastewater with 90% and 80% efficiency, respectively (Li et al. 2016). An activated nylon-membrane with Chitosan modification has been applied in the removal of Cu(II) ions with a high metal affinity (He et al. 2008). This involved three steps:

- Functionalization of nylon membrane through the deposition of a layer of chitosan.
- Polymer stabilization through cross-linked epichlorohydrin and promoting grafting.
- Grafting using iminodiacetic acid.

Fabrication of Chitosan-Nylon-6 was done using the Solution Blow Method with Nylon to chitosan in 6:4 ratios. This has been done through the replacement of nylon-6 with chitosan. This nanofiber membrane was found to be effective in removing Cu(II) ions from wastewater, with a removal efficiency of around 90% and an 8-times recyclability (Kakoria et al. 2021). Triaminotriethoxysilane is grafted on oxidized activated carbon (TATS@AC) through silanization using an ultrasonicated synthesis approach (as shown in Fig. 6.2). This material has been used for the removal of Cd(II) from wastewater (Naushad et al. 2020).

Chitosan-based Schiff bases (CSBs) form an interesting range of biomembranes. As Schiff bases are well-known for their metal-binding properties, these CSBs biomembranes provide an excellent binding and removal medium for heavy metals from wastewater. These CSBs can easily be tuned as per the need for the target metal ions, and metals can be recovered through acid treatment. For example, Fe_3O_4-coated CSBs are magnetically active and can be applied to the recovery of magnetically active ions (Antony et al. 2019). In Indonesia, a group of researchers studied the membrane biofilter made of banana stem for the separation of lead ions. *Acetobacter xylinum* was used for microbial cellulose preparation from the banana stem. Cellulose acetate was extracted to prepare biomembrane (pore size = 5 microns) using dichloromethane, and it was applied to the removal of lead from wastewater. Efficiency has been found to be around 94% for this biomembrane (Sulastri and Rahmidar 2016). Tomato peels were found to be effective biofilters for a wide range of metal pollutants in another set of experiments, including Cr, Ni, As, and Pb. Propanol was used to remove anthocyanins from the peel, and the peels were washed, dried, and used in the separation of metal ions from their mixed aqueous solutions. This holds a better perspective on the application of plant-based biomembranes (Mallampati and Valiyaveettil 2012).

6.3.5 Bioleaching

It is one of the oldest methods for the biological extraction of metals and has been a part of biohydrometallurgy. It has been applied in the mining of copper at the commercial level. Bioleaching emphasizes the application of chemolithotrophic microorganisms, which produce acid. It holds high potential in recovering precious metals in bioremediation (Gu et al. 2018). This is one of the most effective techniques of metal recovery, and metal-loaded bioleachates is suitable for the extraction of metals. Metal leaching in mineral ores by acidophilic iron- and sulfur-oxidizing bacteria is already a research topic in the biomining industry. *Acidithiobacillus ferrooxidans and Acidithiobacillus thiooxidans are two such major bacteria that have been widely used in bioindustry to remove toxic metals from polluted water and sludge. Acidithiobacillus ferrooxidans* mainly targets metal sulphides and causes indirect oxidation and *Acidithiobacillus ferrooxidans* and *Acidithiobacillus thiooxidans* both together directly can directly lead to the direct oxidation of sulphides (Gadd 2000). *Acidithiobacillus thiooxidans* was also used for the recovery of Ni from the electroplating wastewater sludge. One kind of Sulphur-reducing bacterium (SRB) plays a major role in the efficient removal of Ni from wastewater and the metal is extracted in the form of precipitates of NiS and Ni (Yang et al. 2015). Ni removal from wastewater with the application of ZVI (Zero-valent Iron)-SRB was done and it was found that ZVI-SRB had very high efficiency ($> 98\%$) as compared to simple SRB systems (Zhang et al. 2016a). In a similar but novel approach, SRB was applied in the biorecovery of MnS. The application of Mn is very high in semiconductors and optoelectronics. Eriochrome Black-T was used as a complexing agent here (Zhang et al. 2016b).

Various classes and sub-classes of microbes that are used in bioleaching are (Gu et al. 2018):

- **Mesophilic bacteria**: Bacteria that grow best at temperatures ranging from 25 to 35 °C.
- **Acidithiobacillus**: Rod-shaped, Gram-negative, Non-spore producing, Aerobic. They oxidize sulphur compounds like sulphides, sulphur and thiosulphates and the final oxidation products are sulphates. *Acidithiobacillus* are most important in this.
- **Leptospirillum**: Use Fe(II) as an energy source. Can work at lower pH (~ 1.2). Targets metals like U, Mo, Ag and high affinity for Cu. Cannot oxidize sulphur compounds.
- **Thermophilic bacteria and Archae**: They are spore-forming bacteria. Can withstand higher temperatures. Thermophiles at extremely high temperatures are called archaea and they can grow above 60 °C. *Sulpholobus* sp. Can utilize Fe(II), elemental S and Sulphides as a source of energy.
- **Heterotrophic bacteria and fungi**: They primarily rely on organic compounds for energy in metabolism. *Bacillus* (bacteria) and *Aspergillus*, *Pencillium* (fungi) are used in bioleaching.

Printed circuit boards from the chip manufacturing industries are heavily loaded with metals such as Ni, Cu, Zn and Pb. In this sequence, *A. thiooxidans* and *A. ferrooxidans* were used as mixed cultures for bioleaching and the result for extraction was reported to be around 94, 89, 86 and 90, respectively, for each metal. The increased redox potential and lower pH of the filtrate indicated that mixed culture was equally involved in the bioleaching processes (Liang et al. 2010).

6.3.6 Bioremediation

Bioremediation is the in-situ application of plants and related microbes or microorganisms to remove harmful contaminants from the environment. It is useful not only for removing polyaromatic hydrocarbons or organic compounds, but it is also very effective for removing heavy metals. The plants or microbes accumulate heavy metals in their vascular or cellular system through metabolic uptake in their vegetative as well as reproductive parts (Rezania et al. 2016). It is an eco-friendly and cost-effective environmental cleaning technique that serves a dual purpose of water as well as soil cleaning together. The uptake of contaminants follows different mechanisms such as phytoextraction (contaminant uptake through root and accumulation in shoot), rhizodegradation (reduction of heavy metal ions into the rhizosphere via rhizospheric microbes), phytovolatilization (conversion of heavy metals to less toxic forms and release into the environment), and phytostabilization are all processes that occur in plants (reduction and assimilation of heavy metals in the roots of the plants). *Eichhornia crassipes*, an aquatic weed, is well known to uptake Cadmium at even very high contamination (Borker et al. 2013). *Brassica juncea, Sedum alfredii* and *Helianthus annuus* are plants that are well known for the phytoextraction of many heavy metals very efficiently (Milner and Kochian 2008). Phytofiltration is yet another method in which free-floating or submerged plants tend to absorb heavy metals from the water. *Some of the plants that have been extensively studied for their role in the phytostabilization of heavy metals from wastewater include Agratis capillaris, Fetuca rubra, and Lupinus albus* (Kidd et al. 2009).

Hg and Se are two very hazardous metals that need special treatment for their biorecovery. In this regard, phytovolatilization methods are among the safest, as these metals are converted to their volatile form and released into the environment via plant leaves or foliage. *Pteris vittata* is one such plant that can easily take up Arsenic and convert it to a volatile form. The best part about phytovolatilization lies in the fact that the plants are not needed to be harvested and disposed of at regular intervals (Sakakibara et al. 2010). The rhizosphere of plants contains sugar, amino acids, flavonoids and many other components much higher than the rest of the plants. The microbes present here produce many organic chelating compounds such as oxalic acid, citric acid, gluconic acids and different types of surfactants. Siderophore-producing rhizobacteria can increase the bio-uptake of Cr and Pb in plants (Braud et al. 2009); *Gluconacetobacter diazotrophicus* can uptake Zn compounds (Saravanan et al. 2007); some rhizobacteria can increase the uptake of Fe(III) and Mn(IV) through redox-mediated uptake processes (Gadd 2010). Microalgae *Scenedesmus incrassatulus* can easily remove Cr(VI), Cd(II) and Cu(II) from wastewater up-to 78%. Similarly *S. obliqus* and *S. quadricauda* also showed good removal efficiency of Zn(II) (Soeprobowati and Hariyati 2012). Some of the other microalgae which are found effective in heavy metals bioremediation from wastewater have been listed below (Goswami et al. 2021):

- *Chlorella* sp. (Pb, Cd, Cu)
- *Chaetoceros* sp. (Pb)
- *Porphyeridium* sp. (Cd and Cu)
- *Spirulina* (Cd)
- *Chlorella vulgaris* (Ni, Zn, Cd, Cu).

6.3.7 Radionuclides Biorecovery

Radioactive metals are rarely a part of industrial wastewater. But, their presence or their impact can never be ignored as they hold some relevance because of their discharge in wastewater from mining and metallurgical industries. Uranium mining is one of the biggest concerns because of its high radioactivity (Gadd and Pan 2016). The major part of Uranium pollution in industrial wastewater is as U(VI) salts and has easily leaching properties, thereby contaminating the groundwater. The hexavalent state of Uranium is soluble, while its tetravalent state is highly insoluble. Most of the chemical-based techniques for Uranium removal are not much effective, and bioremediation has been found to be the most effective of all the available methods (Williams et al. 2013). One of the most widely used methods for removing Uranium from wastewater is bioconversion of U(VI) to U(IV). However, the presence of oxidizing agents in the atmosphere may interfere with the process and make the bioreduction process a completely useless method. Biomineralization of U(VI) can be therefore counted as a more promising method where the phosphate precipitats U(VI) in the form of Uranyl phosphate complex which is completely immobile. Phosphate is released by bacterial phosphatase activity, and Citrobacter is commonly used for this (Macaskie 2007). Since U(VI) has a high reduction potential, it acts as a suitable electron acceptor at the cathode, and hence MFCs can be one of the techniques for biorecovery of Uranium.

The low concentration of U(VI) and sluggish electrode kinetics of Uranium make a need for nitrate ions at the cathode, and the recovery of U(VI) is activated using denitrifying bacteria that flourish at the cathode and generate phosphatase enzyme. The phosphatase enzyme catalyses the formation of phosphate ions, which then form a complex with U. (VI), and recovery is possible. An MFC has been designed in this regard using *Pseudomonas* sp. at the cathode with glycerol 3 phosphate (Genders et al. 1996; Vijay et al. 2020). *Landoltia punctata* was found effective for the elimination of U(VI) by forming insoluble nano uranium (in IV and VI oxidation state) phosphate in both healthy fronds as well as dead biomass. This remediation process is entirely pH dependent of the wastewater and the initial Uranium concentration, and it has been established that the accumulation capacity of biomass is four times that of living fronds. The process follows the sequence of biosorption followed by bioreduction of Uranium and ultimately biomineralization of Uranium as uranium phosphate (Nie et al. 2017).

6.4 Limitations

Despite the fact that biorecovery processes provide excellent opportunities for heavy metal removal and replenishment from wastewater, their limitations cannot be neglected at all. Some of the important points that are quite important have been discussed below:

- The biosorption process is highly dependent on various factors such as ionic strength, and pH of surrounding ions and suspended impurities in wastewater. The pH needed for the metal ions sorption is majorly neutral; however, the pH of wastewater is generally lower. *Sphaerotilus natans* is a Gram-negative bacterium that has been used in Cu biosorption. High ionic strength negatively impacts the biosorption process (Beolchini et al. 2006). Besides this hardness of water also plays a key role in the biosorption processes. Ca and Mg-induced water hardness has been found to have a significant impact on the biosorption of Fe and Al in industrial wastewater (Lee et al. 2004).
- Biological sulphate reaction, even though it holds multiple advantages over conventional systems, has some serious limitations as well. As it is very well established that this process leads to the formation of metal sulphate, the toxicity of metal sulphates cannot be undermined. If anyhow, these metal sulphates leach into the environment, they can cause serious troubles, especially if the leachates are in the Nanoscale range. The toxicity of nanosized metal sulphates is already well-established for living beings (Kumar and Pakshirajan 2019).
- Bioelectrochemical cells, even though highly clean and viable technology, hold certain limitations. The purity of H_2 generated by microbial electrolytic cells is much higher than in other hydrogen production methods. The H_2 gas produced is accompanied by CO_2. The rate of H_2 generated reduced as the process went on. Most of the BES from the suggested literature showed lower hydrogen generation and decreased current density when applied at the pilot level. Some of the factors that highly affect this phenomenon of the electrochemical system are the geometry of the reactors, material of the electrode, glass fibre-based separators, general electrical resistances and microbial factors that slow down the starting of the reactor (Wilberforce et al. 2020).
- Biomembranes are a promising candidate for separating metal ions from wastewater. There are varieties of pure and composite as well as polymer-grafted biomembranes that are applied for metal ions removal. They are cost-effective, low energy consuming and the cleanest method available. However, the application of biomembranes is limited as the pore diameter of biomembranes ranges around that

of the size of hydrated metal ions. Due to this, sometimes the pores are clogged. Biomembranes need to be cleaned and replenished from time to time to prevent biofouling and membrane protection. Self-cleaning biomembranes and composite biomembranes that prevent bacterial growth will surely be a help in this.

6.5 Conclusions

Metal ions and their biorecovery have been discussed in quite a detail in this chapter. As we have seen, water and metal both hold an essential position in modern times and their demand will keep on increasing with the increasing population. Also, heavy metals are well known for their toxicity and thus, their removal from wastewater is an important thing needed to be taken care of. Several physical and chemical methods for recovering heavy metals from wastewater have already been proposed. These included coagulation, filtration, electrodialysis etc., which were less effective and highly expensive with the production of secondary pollutants/contaminants and sludge. Most of the physical and chemical techniques of biorecovery were not that effective and needed combination of two or more technologies for their success. Biorecovery, which is not an old-school method, played a great role in the metal recovery from wastewater. As we passed through different biorecovery processes, we have come across many methods. BES system has been found to be the most novel and cleanest recovery treatment for metals in wastewater. It depends on the generation of electric current with separation application, hence, serving the dual purpose of cleaning and energy production. It has been proved to be effective for a variety of heavy metals including Fe, Cu, Cd, Zn, As, and Ni. Biomineralization or Bioprecipitation involves the immobilization of metals from their aqueous solutions into solid surfaces or as precipitates. This is primarily used as microbe applications and has been used for metal removal such as Se, Pb, Cd, and others. This process also promotes nanoscale sulphides and oxides formation from the metals and their further applications in environmental cleaning. Biosorption of metals on the surface of biomass is an adsorption-based process where biomass serves as sorbent and metals in wastewater act as sorbate. The interaction may be physical or chemical, or both, depending on the outermost layer of biomass. Biomembranes, as already been discussed, are an old but reliable technique for wastewater treatment and are applied to a variety of metals. Bioleaching is the oldest method for extraction of metals and has been part of the biometallurgy and biomining industries. It uses acidophile and thermophile bacteria for the extraction of metals from their sources. It mainly relies on sulphur-reducing bacteria and Fe, Ni, Zn target metals and radionuclides. Bioremediation applies plants or microbial systems for the removal of harmful metal ions from wastewater. They take up metal ions within their cellular or tissue structure and store them. Metals can be extracted from them after a certain time frame. Radionuclides can also be recovered from their wastewater by the different methods discussed above. All of the methods discussed in this chapter are clean, energy-efficient, and highly specific techniques for heavy metal biorecovery from wastewater. In contrast, each of them comes with one or the other limitations which need to be taken into account before their pilot-level application.

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